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Synthesis and Reduction of Bimetallic Methyl-Bridged Rare-Earth Metal Complexes, $[(C_5H_4SiMe_3)_2Ln(\mu\text{-}CH_3)]_2$ (Ln = Y, Tb, Dy)

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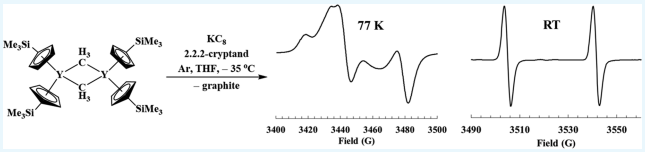
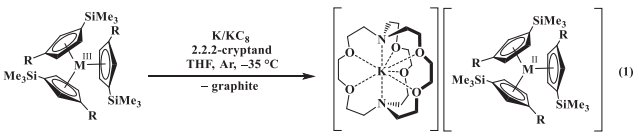
Supporting Information

ABSTRACT: The complexes $[Cp'_2Ln(\mu\text{-}CH_3)]_2$, (Cp′ = $C_5H_4SiMe_3$; Ln = Y, Tb, Dy) were reduced to determine if these methyl-bridged complexes would form mixed valent $4f^n5d^1$ Ln(II)/$4f^n$ Ln(III) compounds or bimetallic $4f^n5d^1$ Ln(II) compounds containing $5d^1$−$5d^1$ metal−metal bonds upon reduction. Reaction of the known bridged-chloride complexes, $[Cp'_2Ln(\mu\text{-}Cl)]_2$, **1-Ln** (Ln = Y, Tb, Dy), with MeLi forms the bridged-methyl complexes $[Cp'_2Ln(\mu\text{-}CH_3)]_2$, **2-Ln**, which were crystallographically characterized for Tb and Dy. KC_8 reduction of **2-Ln** in the presence of 2.2.2-cryptand produced **3-Y**, **3-Tb**, and **3-Dy**, which exhibited intense dark colors and broad absorbance peaks around 400 nm with molar extinction coefficients of 1700, 2300, and 1800 M^{-1} cm^{-1}, respectively, which are characteristics of Ln(II) ions. The dark maroon **3-Y** product had an axial electron paramagnetic resonance spectrum at 77 K (g_1 = 1.99, A_1 = 17.9 G; g_2 = 2.00, A_2 = 17.7 G) and a two-line isotropic spectrum at 273 K (g = 1.99, A = 18.4 G), which indicates that an Y(II) ion is present. Although these results are indicative of Ln(II) ions present in the solution, crystallographic evidence was not obtained to establish the structure of these complexes.



INTRODUCTION

The +2 oxidation state has recently been identified in crystallographically characterizable monometallic molecular complexes of yttrium and all of the lanthanides (except radioactive Pm). This was accomplished using the coordination environment of three trimethylsilyl-substituted cyclopentadienyl ligands, as shown in eq 1.[1−6] Previously, the +2 oxidation state in molecular species had been limited to Eu, Yb, Sm, Tm, Dy, and Nd, which had $4f^{n+1}$ electron configurations obtained by reducing a $4f^n$ Ln(III) precursor.[7−10] Spectroscopic and structural characterizations as well as density functional theory (DFT) calculations have shown that in the trigonal coordination environment of a $[(C_5H_3RR'_3)]^{-3}$ ligand set (R = H, $SiMe_3$, R′ = $SiMe_3$), the new lanthanide ions exhibited a $4f^n5d^1$ ground state and $4d^1$ configuration for yttrium.[1−6] Examples of these new +2 ions are also known with other ligands including $C_5H_3(CMe_3)_2$ (Cp^{tt})$^-$[11,12] and $C_5H_2(CMe_3)_3$ (Cp^{ttt})$^-$,[13,14] the tris(aryloxide) mesitylene ligand, $((^{Ad,Me}ArO)_3mes)^{3-}$ [15,16] and $N(SiMe_3)_2^-$.[17]



R = $SiMe_3$; M = La, Ce, Pr, Nd
R = H; M = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu

The discovery of the $4f^n5d^1$ electron configurations in these new ions presents the possibility of generating complexes which contain Ln−Ln bonds. Traditionally, metal−metal bonding between two lanthanides has been considered unlikely because the 4f orbitals have too limited a radical extension from the nucleus to have significant overlap. However, electrons in d orbitals are well suited to make metal−metal bonds. Since the complexes of new $4f^n5d^1$ Ln(II) ions involve monometallic complexes with sterically crowded ligand environments, they are not ideal for placing two lanthanides in close proximity to bond.

To address this problem, reductions of $[Cp'_2Y(\mu\text{−}Cl)]_2$ and $[Cp'_2Y(\mu\text{−}H)(THF)]_2$ were explored.[18] DFT calculations suggested that reduction of these bimetallic complexes could form complexes containing Y−Y bonds.[18] Although spectroscopic studies, including electron paramagnetic resonance (EPR) spectroscopy and UV−vis spectroscopy, of the reductions of these complexes suggested the formation of an Y(II) ion,[6,18,19] crystallographic evidence was elusive. In the case of complexes containing electron-deficient bridged hydride ligands, $[Cp'_2Y(\mu\text{−}H)(THF)]_2$, only trimetallic tetrahydride complexes, $[K(2.2.2\text{-cryptand})]\{[Cp'_2Ln(\mu\text{-}H)]_3(\mu\text{-}H)\}$ (Ln = Y, Tb, Dy), were isolated from the reduction reactions.[18] The reduction of $[Cp'_2Y(\mu\text{−}Cl)]_2$ provided an EPR spectrum at 77 K consistent with an Y(II) ion. However, this complex was extremely thermally unstable, which prohibited the collection of a room-temperature EPR spectrum, and a crystal structure could not be obtained.

To avoid the possibility of forming such trimetallic hydride-centered products, the reduction of complexes containing electron-deficient methyl-bridged ligands, $[Cp'_2Ln(\mu\text{−}CH_3)]_2$, has been explored and is reported here. Reduction of the known complex, $[Cp'_2Y(\mu\text{−}CH_3)]_2$,[20] is described as well as

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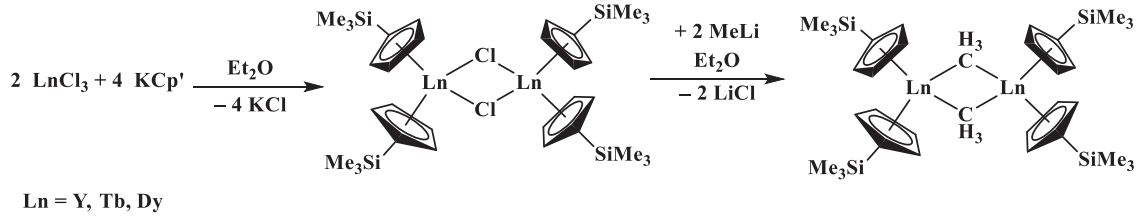
Scheme 1. Syntheses of $[Cp'_2Ln(\mu\text{-}Cl)]_2$, 1-Ln, and $[Cp'_2Ln(\mu\text{-}CH_3)]_2$, 2-Ln {Cp′ = $[C_5H_4(SiMe_3)]$}



analogous reactions of the Tb and Dy analogues, which were synthesized for this study and crystallographically characterized for definitive identification.

RESULTS AND DISCUSSION

Reaction of the known bridged-chloride complexes, $[Cp'_2Ln(\mu\text{-}Cl)]_2$, **1-Ln**, with 2 equiv of methyl lithium generates the bridged-methyl complexes $[Cp'_2Ln(\mu\text{-}CH_3)]_2$, **2-Ln**, needed for this study, Scheme 1 (Ln = Y, Tb, Dy). The previously reported Y complex was identified by ^{1}H NMR spectroscopy,[20] and the paramagnetic Tb and Dy complexes were identified by X-ray crystallography, Figure 1. **2-Tb** and **2-Dy** are isomorphous with **2-Y**. Crystallographic details can be found in the Supporting Information.

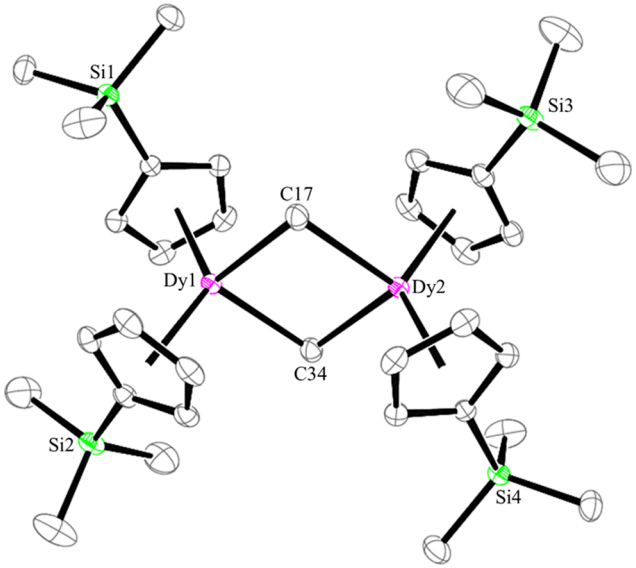


Figure 1. ORTEP depiction of $[Cp'_2Dy(\mu\text{-}CH_3)]_2$, **2-Dy**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

The crystallographic data show that the methyl-bridged complexes, **2-Ln**, have shorter Ln···Ln distances than either the chloride precursors, **1-Ln**, or the tetrahydrofuran (THF)-solvated hydrides, $[Cp'_2Ln(\mu\text{-}H)(THF)]_2$, Table 1.[18] For example, the Tb···Tb distances in the two molecules in the unit cell of **2-Tb** were determined to be 3.5415(5) and 3.5745(4) Å compared to 4.0705(4) and 3.7041(6) Å for **1-Tb** and $[Cp'_2Tb(\mu\text{-}H)(THF)]_2$,[18] respectively. The Ln−X−Ln angles in **2-Ln** were also determined to be the smallest when compared to the chloride and hydride analogues. These were 89.73(8) and 90.17(8)° in **2-Tb** compared to 97.29(2) and 120.7(2)° in **1-Tb** and $[Cp'_2Tb(\mu\text{-}H)(THF)]_2$,[18] respectively. These smaller distances could

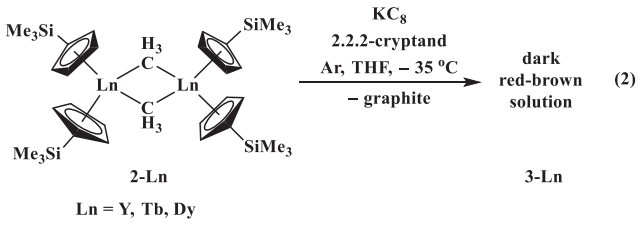
Table 1. Comparison of the Ln···Ln Distances and Ln−X−Ln Angles in 1-Ln, 2-Ln, and $[Cp'_2Ln(\mu\text{-}H)(THF)]_2$

complex	Ln···Ln distance (Å)	Ln−X−Ln angle (deg)
$[Cp'_2Y(\mu\text{-}CH_3)]_2$, **2-Y**[20]	3.5361(9)	89.18(13)
$[Cp'_2Y(\mu\text{-}Cl)]_2$, **1-Y**[21]	4.0792(9)	98.4(1)
$[Cp'_2Tb(\mu\text{-}CH_3)]_2$, **2-Tb**[a]	3.5415(5)	90.17(8)
	3.5745(4)	89.73(8)
$[Cp'_2Tb(\mu\text{-}H)(THF)]_2$[18]	3.7041(6)	120.7(2)
$[Cp'_2Tb(\mu\text{-}Cl)]_2$, **1-Tb**[18]	4.0705(4)	97.29(2)
$[Cp'_2Dy(\mu\text{-}CH_3)]_2$, **2-Dy**[a]	3.5219(5)	90.36(8)
	3.5543(5)	89.70(8)
$[Cp'_2Dy(\mu\text{-}H)(THF)]_2$[18]	3.7042(3)	119.4(14)
$[Cp'_2Dy(\mu\text{-}Cl)]_2$, **1-Dy**[18]	4.0806(5)	97.89(1)

[a]Unit cell contains two molecules.

facilitate an interaction between the two rare-earth ions upon reduction by bringing the metal centers closer to each other.

Reduction of the **2-Ln** complexes with 1 equiv of KC_8 in the presence of 1 equiv of 2.2.2-cryptand (crypt) in THF produced intensely colored red-brown products, **3-Ln**eq 2, typical of crystallographically characterized complexes of rare-earth ions in the +2 oxidation state, eq 1.[2−4,6,18] The EPR spectrum of **3-Y** at 77 K has an axial signal at g_1 = 1.99, A_1 = 17.9 G; g_2 = 2.00, A_2 = 17.7 G, and the room-temperature EPR spectrum has an isotropic signal at g = 1.99, A = 18.4 G (Figure 2). These patterns are consistent with the interaction of an unpaired electron with a ^{89}Y nucleus (100% abundant I = 1/2) and are characteristic of Y(II) complexes (Figure 2).[3−5,11]



The UV−vis spectra of **3-Y**, **3-Tb**, and **3-Dy**, Figure 3, show broad absorbance peaks at 420, 405, and 410 nm with molar extinction coefficients of approximately 1700, 2300, and 1800 M^{-1} cm^{-1}, respectively, based on the moles of metal present in the sample. The ε values are lower estimates that are based on the amount of **2-Ln** used to form the sample assuming complete reduction to **3-Ln**. In comparison, [K(crown)]-$[Cp'_3Y]$ and [K(crypt)]$[Cp'_3Y]$ have absorptions at 530 nm (ε = 2500 M^{-1} cm^{-1})[6] and 520 nm (ε = 4500 M^{-1} cm^{-1}), respectively.[3,4] The data on **3-Ln** can also be compared with those from the reductions of $[Cp'_2Y(\mu\text{-}H)(THF)]_2$, 794 nm ($\varepsilon$ = 1000 M^{-1} cm^{-1}), $[Cp'_2Tb(\mu\text{-}H)(THF)]_2$, 837 nm ($\varepsilon$ = 840 M^{-1} cm^{-1}), and $[Cp'_2Dy(\mu\text{-}H)(THF)]_2$, 715 nm ($\varepsilon$ = 640 M^{-1} cm^{-1}), Figure 4.[18]

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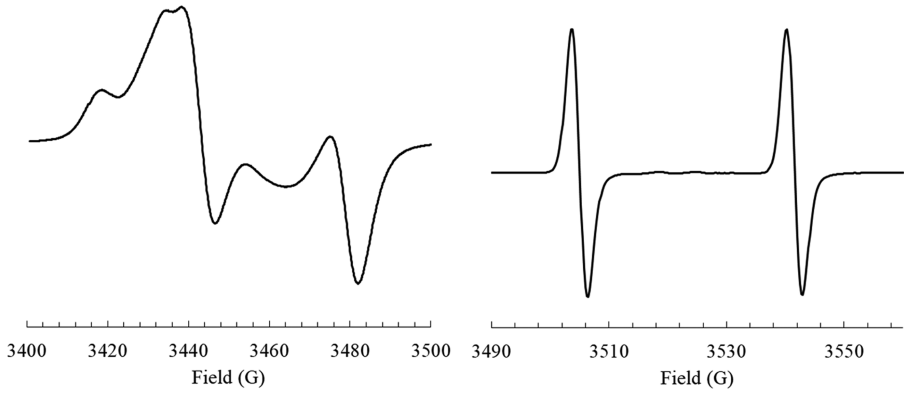

Figure 2. EPR spectra of **3-Y** at 77 K (left; g_1 = 1.99, A_1 = 17.9 G; g_2 = 2.00, A_2 = 17.7 G) and 273 K (right; g = 1.99, A = 18.4 G).

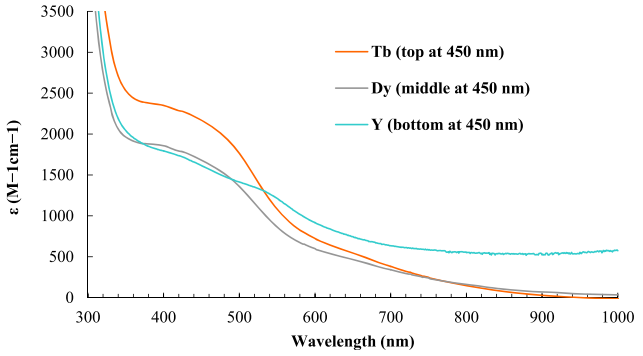

Figure 3. UV−vis spectra of **2-Ln** reduction products: **3-Y** (λ = 420 nm; ε = 1700 M^{-1} cm^{-1}), **3-Tb** (λ = 405 nm; ε = 2300 M^{-1} cm^{-1}), and **3-Dy** (λ = 410 nm; ε = 1800 M^{-1} cm^{-1}).

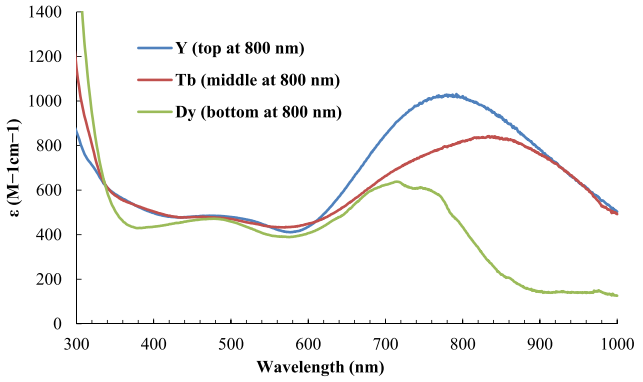

Figure 4. UV−vis spectra of $[Cp'_2Ln(\mu\text{-}H)(THF)]_2$ reduction products: **Y** (λ = 794 nm; ε = 1000 M^{-1} cm^{-1}), **Tb** (λ = 837 nm; ε = 840 M^{-1} cm^{-1}), and **Dy** (λ = 715 nm; ε = 640 M^{-1} cm^{-1}).

The dark-colored solutions of **3-Ln** maintained their color in solution at −30 °C for several days, but they did not yield crystalline products suitable for definitive characterization by X-ray diffraction. Attempts to make analogues with 18-crown-6 instead of crypt were similarly unsuccessful.

CONCLUSIONS

Although the bridged-methyl complexes $[Cp'_2Ln(\mu\text{-}CH_3)]_2$, **2-Ln**, can be reduced to form dark solutions with EPR and UV−vis spectroscopic features consistent with Ln(II), isolation of crystallographically characterizable Ln(II) complexes has not been possible. These results indicate that the bis(Cp′) coordination environment is not optimum for crystallizing bimetallic complexes with a rare-earth metal in the +2 oxidation state.

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. UV−vis spectra were collected at 298 K using a Jasco V-670 absorption spectrometer. EPR spectra were collected using X-band frequency (9.3−9.8 GHz) on a Bruker EMX spectrometer equipped with an ER041XG microwave bridge, and the magnetic field was calibrated with DPPH (g = 2.0036). Infrared (IR) transmittance measurements were taken as compressed solids on a Cary 630 spectrophotometer with a diamond ATR attachment. 2.2.2-Cryptand (Sigma-Aldrich) was placed under vacuum (10^{-3} Torr) overnight before use. The solvent was removed under vacuum from a solution of methyl lithium in Et_2O (Sigma-Aldrich) to isolate it as a white powder. Anhydrous $LnCl_3$ (Ln = Y, Tb, Dy),[22] KC_8,[23] and $KC_5H_4(SiMe_3)$ (KCp′)[24] were prepared according to the literature. $[Cp'_2Ln(\mu\text{-}Cl)]_2$ (Ln = Y,[21] Tb,[18] Dy[18]), **1-Ln**, and $[Cp'_2Y(\mu\text{-}CH_3)]_2$[20] were prepared by a modification of the literature procedure.

$[Cp'_2Dy(\mu\text{-}CH_3)]_2$, 2-Dy. A solution (−30 °C) of **1-Dy** (150 mg, 0.158 mmol) in Et_2O (5 mL) was slowly added to a −30 °C slurry of MeLi (12 mg, 0.546 mmol) in Et_2O (5 mL). The total volume of the solution was increased to 20 mL with cold Et_2O. The slightly cloudy colorless solution was allowed to warm to room temperature and stirred overnight. The volatiles were removed from the solution in vacuo. The product was extracted into hexane (10 mL) and then centrifuged to remove white solids, presumably LiCl. The white solids were washed with hexane (5 mL) twice. The volatiles were removed from the hexane solution to isolate a white powder. The white powder was extracted into hexane (10 mL) again, and any insoluble materials were discarded. The volatiles were removed from the hexane solution to isolate **2-Dy** as a white powder (123 mg, 0.136 mmol, 86%). X-ray quality crystals were grown from a concentrated hexane solution at −30 °C. IR: 3079(w), 2950(w), 2885(w), 1440(w), 1360(w), 1343(w), 1242(s), 1176(m), 1038(s), 905(m), 890(w), 829(s), 772(s), 751(s), 688(m). Anal. calcd for $C_{34}H_{58}Dy_2Si_4$: expected = C, 45.17; H, 6.47. Found: C, 41.97;

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H, 6.23. The low value suggests incomplete combustion, as observed in other cases.[1,25−28] The found CH ratio of $C_{34}H_{60.1}$ is consistent with the formula.

[Cp′$_2$Tb(μ-CH$_3$)]$_2$, 2-Tb. In a procedure analogous to the synthesis of **2-Dy**, **1-Tb** (150 mg, 0.161 mmol) and MeLi (11 mg, 0.482 mmol) were combined in Et_2O (20 mL) to isolate **2-Tb** as a white powder (133 mg, 0.148 mmol, 92%). X-ray quality crystals were grown from a concentrated hexane solution at −30 °C. IR: 3075(w), 2951(w), 2880(w), 2814(w), 2768(w), 1711(w), 1640(w), 1604(w), 1537(w), 1442(w), 1409(w), 1359(w), 1308(w), 1242(m), 1178(m), 1130(w), 1038(s), 904(m), 888(w), 830(s), 763(s), 751(s), 687(m). Anal. calcd for $C_{34}H_{58}Tb_2Si_4$: expected = C, 45.52; H, 6.52. Found: C, 41.93; H, 5.90. The low value suggests incomplete combustion, as observed in other cases.[1,25−28] The found CH ratio of $C_{34}H_{57}$ is consistent with the formula.

Reduction of 2-Y. In an argon-filled glovebox, a colorless solution of **2-Y** (106 mg, 0.140 mmol) and crypt (53 mg, 0.141 mmol) in THF (2 mL) was chilled to −30 °C. The solution was passed through a KC_8 column chilled to −30 °C, and a dark red-brown solution, **3-Y**, resulted. EPR spectra were obtained at 77 K and room temperature. UV−vis (THF) λ_{max} = 420 nm; ε = 1700 M^{-1} cm^{-1}.

Reduction of 2-Dy. In a procedure analogous to the reduction of **2-Y**, **2-Dy** (198 mg, 0.219 mmol) and crypt (83 mg, 0.219 mmol) were combined in THF (2 mL) and passed through a KC_8 column to form a dark red-brown solution, **3-Dy**. UV−vis (THF) λ_{max} = 414 nm; ε = 1800 M^{-1} cm^{-1}.

Reduction of 2-Tb. In a procedure analogous to the reduction of **2-Y**, **2-Tb** (200 mg, 0.224 mmol) and crypt (84 mg, 0.224 mmol) were combined in THF (2 mL) and passed through a KC_8 column to form a dark red-brown solution, **3-Tb**. UV−vis (THF) λ_{max} = 406 nm; ε = 2300 M^{-1} cm^{-1}.

X-ray Crystallographic Data. Crystallographic informations for complexes **2-Tb** (1871704) and **2-Dy** (1871703) are in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02665.

Crystallographic details, selected bond distances and crystallographic data (CIF) for **2-Tb** and **2-Dy** (PDF)

Structure factors for datablocks mtd23 and mtd24, respectively (PDF) (PDF)

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Notes

The authors declare no competing financial interest.

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